

Title:

"Desulphurization of ferrous materials using sodium silicate"



Cross-reference to related applications: None

5 **Federally sponsored statement: N/A**

Reference listing: None

Description

FIELD OF THE INVENTION

The present invention relates to (1) the use of a sodium compound as the primary desulphurizing reactant in a reactive desulphurizing agent, (2) ~~to an~~the option of including other desulphurizing reactants obtained from other reactive alkali oxides, alkaline oxides or other chemical compounds and metallic solids, (3) the method for producing the sodium-based reactive desulphurizing agent, (4) the process of applying the sodium-based reactive desulphurizing agent to a molten ferrous material and (5) the process for the deoxidation or reduction of the iron oxide in a molten ferrous material.

10 BACKGROUND OF THE INVENTION

Ample agreement exists on the growing need for low sulphur steels. In most types of steels, the presence of sulphur above 0.015% is undesirable. The increasing stringent requirement for better desulphurization of steel is attributed to the need for producing high strength low alloy steel and steels resistant to hydrogen induced cracking. In addition, even minute contents of sulphur has pernicious effects on the manufacturing and finishing of steel products, such as brittle fractures in welding and fabrication, a tendency to separate along grain boundaries when stressed or deformed at temperatures near the melting point during the hot rolling phase in sheet steel processing, and even the influences on as-cast and the processing characteristics of the steel in terms of the workability of surface finish.

20 The desulphurizing of molten ferrous materials comprises thoroughly permeating the molten material with a reactive desulphurizing agent consisting of (1) metal oxides for replacing

the sulphur from the iron and for providing the flux required to float out the spent reactants and (2) the addition of solid metals to complete the deoxidization or reduction the iron. U.S. Pat. No. 4,014,685 teaches the four essential factors, for achieving good desulphurization in either a molten iron or steel, using a reactive desulphurizing agent. The factors are (1) high

5 desulphurizing agent basicity, (2) high temperature on desulphurizing agent contact with the molten material, (3) low oxygen potential and (4) high desulphurizing agent fluidity.

~~Furthermore, it has also been demonstrated that the rate of desulphurization increases when the molten metal and the reactive desulphurizing agent are strenuously agitated or perturbed to enhance the intimate contact between the reactive desulphurizing agent and the~~

10 ~~molten metal. Prior art related to enhancement of the desulphurization process, U.S. Pat. No. 6,383,249, U.S. Pat. No. 5,021,986, U.S. Pat. No. 4,832,739, and U.S. Pat. No. 4,315,773, teaches the method of incorporating a gas-evolving component in the reactive desulphurizing agent. The gas-evolving component releases the gas at the moment the reactive desulphurizing agent comes in contact with the molten ferrous material.~~

15 ~~The gas released in the interior of the molten ferrous material forms gas bubbles that expand rapidly under the effect of the increased temperature brought about by the contact of the reactive desulphurizing agent with the molten ferrous material. The gas bubbles, being of a lesser density, rise through the molten ferrous material. As the gas bubbles percolate or permeate through the molten, collisions take place between bubbles, and the colliding bubbles combine to~~

20 ~~form bigger bubbles. In effect, the volume of the expanding gas bubbles provides the means for increasing the mobility or activity of the reactant metal oxides and also increases the contact area between the reactant oxides in the reactive desulphurizing agent and the molten ferrous material. The increase in both, the mobility of the reactant oxides and the contact area, increases both the~~

~~rate of desulphurization and amount of sulphur removed from the molten ferrous material.~~

~~However, none of these examples given above advance the art of combining the gas-evolving compounds and the desulphurizing reactant compounds in reactive desulphurizing agent.~~

Over the past several decades, a multitude of methods and processes have been set forth
5 for the desulphurization of ferrous molten materials. Most of these methods are based on the
reactions of a lime, fluorspar, aluminum oxide, alkali and alkaline metals or alloys, as well as the
use of other reactants. An example of these methods is in U.S. Pat. No. 3,779,739, which teaches
the art of desulphurization using calcium oxide and aluminum oxide or calcium oxide and
calcium fluoride, wherein the calcium oxide increases the basicity of the desulphurizing agent
10 and the aluminum oxide and calcium fluoride increase the fluidity of the desulphurizing agent.
Magnesium oxide has also been advanced in the art of desulphurizing ferrous materials,
specifically metallic magnesium in U.S. Pat. No. 6,383,249.

Sodium, like magnesium, is a highly reactive metal, thus a high-performing desulphurizer
that allows for a very high sulphur replacement in molten ferrous materials. However, because of
15 its high reactive property, metallic sodium is highly unstable at ambient temperatures and
violently ~~unstable~~ reactive at the temperatures of a molten ferrous material and thus vaporizes
~~quickly~~ explosively on contact with molten ferrous materials, hence metallic sodium, by itself, is
ineffectual in removing sulphur. A preferred composition for the effective use of sodium as a
desulphurizer is a chemical compound, such as in an oxidized state in combination with a flux-
20 enhancing compound. A far-reaching attractive feature in advancing the art of using sodium over
magnesium as a desulphurizer is the availability of sodium compounds at a significantly lower
cost.

The art of using sodium oxide, derived from sodium carbonate, as a reactant in a desulphurizing agent is described in U.S. Pat. No. 4,014,685, U.S. Pat. No. 4,956,010, and U.S. Pat. No. 4,353,739. In none of these examples, where the art of using sodium oxide as a reactant in a reactive desulphurizing agent is put forth, is the art advanced wherein sodium silicate is used as the source of the sodium oxide desulphurizing reactant. Nor is a mention made on the preferred form for using a sodium silicate composition as the sole desulphurizer reactant in a desulphurizing agent.

By itself, the melt point of SiO_2 is about 1580°C . However, once the SiO_2 is mixed or combined with other oxides such as Na_2O , the melt point of the resulting composition is much lower, around 700°C . The low melt point is an important and practical industrial property. On contact with the molten ferrous material, less thermal energy is required to dissolve the solid sodium silicate reactive desulphurizing agent; thus, less caloric energy is necessary to maintain the ferrous material in its molten state as the sulphur replacement progresses. Hence, the use of sodium silicate as a desulphurizing agent is an efficient and effective method for removing sulphur from ferrous materials.

SUMMARY OF THE INVENTION

A method is disclosed for removing sulphur in molten ferrous materials using a sodium-based reactant in a reactive desulphurizing agent. The preferred reactant in the reactive desulphurizing agent is sodium silicate. A lime, dolomite, an alumina or mixtures thereof, may optionally be added to enhance the replacement of the sulphur and control of the fluidity of the spent reactants in the molten ferrous materials.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

According to the present invention, a reactive desulphurizing agent is sodium silicate, wherein the chemical composition of the sodium silicate comprises of y parts of SiO_2 to x parts of Na_2O and wherein, yet further, the ratio, y/x, is anywhere from 0.5 to 5. The SiO_2 and the Na_2O are fused at high temperatures. In the preferred embodiment of the invention the fusion takes place in a glass tank at temperatures from 900 to 1500°C. Other types fusion units, such as a rotary furnace, can also be used for the present invention provided the end results are consistent with the intent and scope of the invention.

The sodium silicate reactive desulphurizing agent is ~~combined~~ brought into intimate contact with sulphur-laced molten ferrous materials. In the preferred embodiment of the invention, the molten ferrous material is drawn, in predetermined amounts, and laid in a layer to cover the surface of a desulphurizing vessel. The layer of molten ferrous material is then covered by a predetermined amount of sodium silicate reactive desulphurizing agent. The process is repeated at least once until all the molten ferrous material available is desulphurized within the volume capacity of the vessel. As the desulphurization of the molten ferrous materials progresses, the spent reactants fluidize the surface and are removed from the desulphurizing vessel. To complete the reduction or deoxidation of the iron, a metallic solid is introduced into the molten ferrous material. In the preferred embodiment of the invention the metallic solid is an aluminum rod.

In another embodiment of the invention, the reactants of the reactive desulphurizing agent comprise: sodium silicate, as prepared in the preferred embodiment, and oxides of calcium, magnesium and aluminum. The preferred materials for said oxides are a lime compound such as

limestone, dolomite and an alumina composite, respectively. The preferred composition of the reactive desulphurizing agent comprises:

Na_2O — from about 4 to about 50%

SiO_2 — from about 4 to about 50%

5 CaO — is $\leq 25\%$

MgO — is $\leq 4\%$

Al_2O_3 — is $\leq 14\%$

CO_2 — is $\leq 42\%$

10 The said preferred reactive desulphurizing agent composition is combined with the molten ferrous materials, using the procedure as described in the preferred embodiment of the invention. On contact with the molten ferrous, the temperature of said reactive desulphurizing agent rises, causing the limestone and dolomite to release carbon dioxide gas into the molten ferrous material. As the carbon dioxide gas permeates through the molten ferrous material, the sulphur replacement activity of the metal oxide reactants is enhanced.

15 The released carbon dioxide gas forms bubbles within the molten ferrous material and rise to the surface of the desulphurizing vessel. As the gas rise through the molten ferrous material, the bubbles collide and combine to form bigger bubbles with increasing volumes. The increased gas volumes increase the surface area between the desulphurizing reactants and the molten ferrous material, thus increasing the amount and rate of sulphur replacement in the iron.

20 We suspect, that the rising bubbles of carbon dioxide contribute to the upward fluidity of the

~~spent desulphurizing reactants, thus removing the sulphur from the iron and prevent the resulphurization of the ferrous material.~~

According to the invention, the preferred composition of the reactants in reactive desulphurizing agent, without the carbon dioxide comprises:

5	Na_2O	from about	7 to about	50%
	SiO_2	from about	7 to about	50%
	CaO	is	\leq	45%
	MgO	is	\leq	8%
	Al_2O_3	is	\leq	25%

10 These and other advantages and features of the present invention will be more fully understood with the examples thereof.

EXAMPLE 1

A reactive desulphurization agent, based on sodium, was prepared from a composition of a sodium silicate and oxides of aluminum, magnesium and calcium. The parts ratio of the silicon
15 oxide to the sodium oxide was 2.3:1, resulting in a sodium silicate composition with about 29.7%, by weight, of sodium oxide and about 71.3%, by weight, of silicon oxide. In addition to the sodium silicate composition, alumina, dolomite and lime where added in the amounts given in Table 1. The components where combined using a blade mixer in three approximately equal batches to obtain consistent mixtures. The weight percentages of the oxides in the unspent
20 reactive desulphurizing agent are listed in Table 2. After mixing, the components were placed super-sacks and shipped to the site of the Basic Oxygen Furnace (BOF).

Table 1.

Desulphurizing Agent Component Weight	
Component	Kg
Sodium silicate	234.5
Alumina	284.1
Dolomite	218.8
Lime	535.4

Total 1272.8

Table 2.

Desulphurizing Agent Composition (pbw)	
Reactive Oxides	<u>Percent by Weight</u>
CaO	52.9 <u>53.33</u> %
Na ₂ O	6.2 <u>7.19</u> %
MgO	4.1 <u>5.70</u> %
Flux Enhancers	<u>Percent by Weight</u>
Al ₂ O ₃	20.0 <u>18.35</u> %
SiO ₂	16.8 <u>15.42</u> %
Total	100.00%

5

At the BOF site, initially, 70 metric tons of molten steel were drawn into a tap vessel and covered by 400 kg of the sodium-based reactive desulphurizing agent, as described in Table 1. An additional 70 metric tons of molten steel were again drawn into the tap vessel and again covered the sodium-based reactive desulphurizing agent. The controls parameters were

maintained constant to provide oxygen at 356ppm. A solid metallic aluminum wire was injected into the molten steel to deoxidize the iron oxide, with the oxygen reduced to 2.5ppm. During the desulphurization of the molten steel, neither the presence of toxic vapors nor the presence of sodium where detected in the immediate surrounding area. The spent reactants of the reactive desulphurizing agent remained dissolved and fluid during the desulphurization process.

Measurements performed on samples taken prior and after desulphurization indicate that the sulphur content of the molten steel was reduced from 0.012% to about 0.00088%.

EXAMPLE 2

In the second example, the sodium-based reactive desulphurizing agent based again was prepared from a sodium silicate and oxides of aluminum, magnesium and calcium. The ratio of the silicon oxide to the sodium oxide was maintained as before, 2.3:1, resulting in a sodium silicate composition with about 29.7%, by weight, of sodium oxide and about 71.3%, by weight, of silicon oxide. However the amounts the sodium silicate composition, alumina, dolomite and lime added were slightly change, as given by weight amounts in Table 3. As before, the components where combined using a blade mixer in successive batches. The batch weights for this example were not reported. The weight percentages of the oxide in the final sodium-based reactive desulphurizing agent composition are listed in Table 4. After mixing, the components were placed super-sacks and shipped to the BOF site.

Table 3.

Desulphurizing Agent Component Weight	
Component	Kg
Sodium silicate	225.8
Alumina	364.8
Dolomite	200.9
Lime	408.5

Total 1200.0

5

Table 4.

Desulphurizing Agent Composition (pbw)	
Reactive Oxide	<u>Percent by Weight</u>
CaO	45.50%
Na ₂ O	7.00%
MgO	7.00%
Flux Enhancers	<u>Percent by Weight</u>
Al ₂ O ₃	25.00%
SiO ₂	15.50%

Total 100.00%

Essentially the desulphurization procedure at the BOF site, as outlined in Example 1, was repeated in this example, with the exception that the oxygen levels were lower both during the

desulphurization phase and the deoxidation phase. Initially, 70 metric tons of molten steel were drawn into a tap vessel and covered by 400 kg of the sodium reactive desulphurizing agent, as described in Table 1. An additional 70 metric tons of molten steel were again drawn into the tap vessel and again covered with a layer of the sodium reactive desulphurizing agent. The controls

5 parameters were maintained constant to provide oxygen at 226ppm. Metal aluminum wire was injected into the molten steel to deoxidize the iron oxide. In this example, the oxygen was reduced to 1.7ppm. During the process, neither the presence of toxic vapors nor the presence of sodium were detected in the immediate surrounding area. The spent reactants of the reactive desulphurizing agent, as before, remained dissolved and fluid during the desulphurization
10 process. Measurements performed on samples taken prior and after desulphurization indicate that the sulphur content of the molten steel was reduced from 0.0153% to about 0.00135%.

A further variation of the process consists of a number of sequential charges of lesser amounts of the molten steel charge and provide said molten charge with a layer of the reactive desulphurizing agent, wherein each layer of the reactive desulphurizing is in intimate contact
15 with the molten material.

It will be appreciated that the instant specifications and claims are set forth by way of illustrating and not limiting the present invention, and that various modifications and changes may be made without departing from the spirit, scope and intent of the present invention.

Claims

What is claim is:

1. A method for desulphurizing a molten ferrous material, comprises a reactive desulphurizing agent, said reactive desulphurizing agent further comprises of desulphurizing reactants, wherein at least one desulphurizing reactant contains a sodium compound.
2. A method as defined in claim 1, wherein the sodium compound is in a sodium silicate composition.
3. A method as defined in claim 2, wherein the sodium silicate composition comprises:
 - a. a sodium oxide, Na_2O ; and a silicon oxide, SiO_2 ; wherein further,
 - b. x parts of Na_2O and of y parts of SiO_2 ; wherein yet further,
 - c. the ratio, y/x , is anywhere from 0.5 to 5.
4. "Amended" A process of claim 43, wherein the fusion of the sodium oxide and the silicon oxide takes place in a glass tank.
5. "Amended" A process of claim 43, wherein the fusion of the sodium oxide and the silicon oxide takes place in a rotary furnace.
6. A method as defined in claim 1, wherein the reactive desulphurizing agent comprises of a sodium silicate and at least one other non-sodium desulphurizing reactant.

7. A method as defined in claim 6, wherein the non-sodium desulphurizing reactants, in the reactive desulphurizing agent, are selected from a group of alkali earth metal compounds, alkaline metal compounds and other metals, compounds, composition and combinations thereof.

5 8. ~~“Deleted”~~ A method as defined in claim 7, wherein at least one of the non-sodium desulphurizing reactants, the reactive desulphurizing agent, may comprise of at least one gas-evolving compound.

9. “Twice Amended” A method as defined in claim 8, wherein the desulphurizing agent comprises of a sodium silicate and non-sodium
10 desulphurizing reactants, wherein the sources for said non-sodium desulphurizing reactants are obtained from calcined materials: a lime, dolomite and an alumina.

10. A method as defined in claim 9, wherein lime, dolomite and alumina provide:

- a. calcium oxide;
- b. magnesium oxide; and
- 15 c. aluminum oxide.

11. “Seven Times Amended” A method as defined in claim 9, wherein the desulphurizing agent comprises a solid mixture of from about 47 to about 50% by weight of sodium oxide, from 47 to about 50% by weight of silicon oxide, less than or equal to about 2545% by weight of calcium oxide, less than or equal to
20 about 48% by weight of magnesium oxide, and less than or equal to about 1425%

by weight of aluminum oxide and less than or equal to about 42% by weight of carbon dioxide.

12. "Amended" A method according to claim 9, wherein the reactive desulphurizing agent is placed in intimate contact with a molten ferrous material for the purpose of replacing the sulphur contaminant in the iron.

13. "Deleted" A method as defined in claim 8, wherein the gas-evolving compound releases the gas after the reactive desulphurizing agent is placed in intimate contact with the molten ferrous material.

14. "Deleted" A method as defined in claim 9, wherein the lime and dolomite comprise gas-evolving compounds, wherein after intimate contact with the molten ferrous material, gas comprising of vaporized carbon dioxide, less than 42% of the desulphurizing agent, is released into the molten ferrous material.

15. "Deleted" A method as defined in claim 13, wherein the sulphur replacement reactants in the reactive desulphurization agent in the molten ferrous material comprise from 7 to about 50% by weight of sodium oxide, from 7 to about 50% by weight of silicon oxide, less than or equal to about 45% by weight of calcium oxide, less than or equal to about 8% by weight of magnesium oxide, and less than or equal to about 25% by weight of aluminum oxide.

16. "Amended" A method according to claim 13, wherein at least one metallic solid is introduced into the desulphurized molten ferrous material to deoxidize or reduce the iron in the molten ferrous material.

17. A method as defined in claim 1, wherein the reactive desulphurizing agent is placed in intimate contact with molten ferrous materials.

18. A method according to claim 17, wherein at least one metallic solid is introduced into the desulphurized molten ferrous material to deoxidize or reduce the iron in the molten ferrous material.

19. A method as defined in claim 1, wherein the ferrous material is selected from a group comprising: iron, pig iron, iron alloy, steels, mixtures thereof and other ferrous materials and wherein said ferrous material is contaminated with sulphur.

20. "New" A method derived from claim 1, wherein the desulphurizing agent is also a fluxing agent.

21. "New" A method as defined in claim 20, wherein the fluxing agent enhances the process of replacing of sulphur in the ferrous material.

Abstract

The invention relates to a method for the preparation of a sodium-based reactive desulphurizing agent for use in molten ferrous materials. The sodium in the reactive desulphurizing agent is a sodium silicate, a composition comprising of Na_2O and SiO_2 . In a second embodiment of the invention, the sodium silicate reactive desulphurizing agent also comprises of an alkali or an alkaline material or other materials, such as oxides of calcium, aluminum and magnesium.

Preferred raw materials for the oxides of calcium, aluminum and magnesium are, respectively, lime, alumina and dolomite. The premixed solid reactive desulphurizing agent is brought in

contact with the molten ferrous material, allowing the desulphurization or the double replacement of the iron sulphur to take place and produce a ferrous oxide. The sodium in the reactive desulphurizing agent is rendered resistant to combustion or evaporation on contact with the molten ferrous materials by the flux activity of the silica. A metallic solid, such as aluminum, is introduced into the molten ferrous material to complete the reduction of the ferrous oxide.